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(54) Title: HEAT CURABLE INK-JET LEGEND INK FOR PRINTING ON PRINTED CIRCUIT BOARDS

(57) **Abstract:** The invention relates to a heat curable ink composition for printing on printed circuit boards using an ink jet printer, comprising at least one non-aqueous solvent, at least one pigment, a melamine based resin system, at least one additive, and at least one dispersing agent. The melamine based resin system comprises a crosslinking agent and a polymer capable of reacting with said crosslinking agent. The invention also relates to a method for printing a legend onto a printed circuit board comprising ink jet printing the heat curable ink composition onto a printed circuit board.

HEAT CURABLE INK-JET LEGEND INK FOR PRINTING ON PRINTED CIRCUIT BOARDS

FIELD OF THE INVENTION

The present invention relates to the field of printed circuit boards (PCB's). More specifically, the present invention relates to heat curable legend ink for printing on PCB's using an ink jet printer.

BACKGROUND OF THE INVENTION

Printed circuit boards serve to interface and connect the various components in electronic devices. The production of a PCB is a multi-step process that includes marking the PCB with a legend showing the location of each part on the board, the identification number, and the polarity of the part. Other markings may also be necessary.

Typically, the PCB legend is formed through screen-printing, using a screen stencil and a curable (heat, UV, or EB) ink that is pressed through the stencil. Screen-printing requires making a new stencil for printing every type of printed board. Therefore, in the case of printed boards produced in a small lot, the printing cost per printed circuit board is greatly increased. Screen-printing has other disadvantages such as the minimal achievable pitch i.e. inability to produce legible characters of small dimensions (e.g. 0.5mm characters).

Ink jet printing provides an ideal solution to the aforementioned problems. Ink jet printing is a process whereby an image is printed directly from an electronic file onto a substrate, without contact between the printing device and the substrate. Printing occurs via projection of a stream of ink droplets to a surface while controlling the direction of the stream so that the droplets are caused to form the desired printed image on the surface. An ink jet printer for use in printing legends on printed circuit boards is described in PCT/IL01/00596, entitled, "Jet Print Apparatus and Method for Printed Circuit Board Manufacture". Ink jet printing of PCB's provides the following advantages: (1) there is no need to produce a stencil for each type of PCB; (2) direct digital printing enables digital compensation and correction of distortion of the PCB; (3) the demanding step of placing the screen over the PCB (in screen printing) is avoided; (4) small characters, not legible using screen printing, may be printed by the

precise drop placement of ink jet printing.

Commercial legend inks for PCB's are typically viscous pastes which are comprised of curable polymers, oligomers, monomers, and solid particulate fillers with particle size of about 5 microns. These inks are not appropriate for use in an ink jet printer. An ink jet ink needs to have an appropriate viscosity and surface tension in order to enable jetting. The ink must have a particle size small enough so as to enable passage through the ink jet nozzle without clogging. Also, the printed legend must be able to withstand immersion in a solder bath of about 250 deg. C without yellowing. In general, the legend must conform to the standards set out in IPC-TM-650 test methods (the Institute for Interconnecting and Packaging Electronic Circuits) and to legibility guidelines set out in IPC-A600.

Conventional ink jet inks form a solid layer on the substrate after printing, by evaporation of the solvent in which the pigment is dispersed, or by using a phase change ink, or even by UV curing while using suitable monomers and oligomers. However, conventional ink jet inks, which are designed for graphic arts or even for textile, are not suitable for printing onto PCB surfaces, due to the very extreme conditions which the printed pattern is exposed to, such as very high temperatures in the solder bath, or presence of very aggressive solvents, which could dissolve the printed pattern, or could decrease the adhesion of the printed legend to the PCB. Improved printed pattern resistance can be achieved by using a curing mechanism, which enables formation of chemical links between the printed patterns and the substrate. For example, U.S. Pat. No. 6,140,391 to Zou et al. relates to a reactive jet ink composition suitable for application onto a substrate (intended for printing on sausages) comprising an ink carrier, a colorant, a polyol, an aldehyde-based cross-linking agent (a melamine formaldehyde resin or other aldehyde resin), and an acid catalyst that promotes a reaction between the cross-linking agent, the polyol, and the substrate. The invention is based on chemical reactions that take place between the substrate and the cross-linking agent, and is therefore limited to those substrates which contain chemical moieties capable of reacting with the resins in the ink, such as cellulose derivatives. The ink is therefore not suitable for use with PCB's. In addition, the acid catalyst contained in the ink, which is required for the appropriate curing of the ink at low temperatures, may react prematurely due to prolonged operation in the print head, resulting in undesirable curing of the ink. This results in increased ink

viscosity and may lead to blockage of the print head nozzles. Thus, the use of the catalyst prevents the possibility of using the ink at elevated temperatures. In addition, curing can occur in the ink container, prior to introduction into the printer.

Ink jet inks used in graphic arts typically contain 3 to 8% pigment dispersed in aqueous solutions. The presence of higher pigment loading is avoided because of nozzle clogging problems. However it is desirable to have a higher loading of pigment in the ink, particularly in the case of white pigments in order to obtain sufficient hiding power and optical density. In addition, the water-based nature of many inks may contribute to corrosion of metallic components within the printhead.

It is therefore the object of the present invention to provide a heat curable ink for ink jet printing onto PCB's that overcomes the aforementioned problems including those associated with the extreme conditions which the PCB and the printed legend are exposed to, and also overcomes the premature curing by the use of a basic inhibitor that volatizes at curing temperatures (130-150C), thereby enabling curing and adhesion to the PCB. The ink has the advantage of having a low viscosity at high temperatures and a high viscosity at room temperature, thus enabling good jetting from the print head (which requires low viscosity). Upon contact with the PCB, the ink cools, and the viscosity increases, thus enabling the droplets of ink to be fixed in position. The ink of the present invention meets the PCB legend ink test requirements of the ICP and displays excellent adhesion to the printed circuit board. The ink also exhibits resistance to various solvents that are part of the flux composition (e.g. iso-propyl alcohol), is very stable at high temperatures, and can withstand dipping in a solder bath of 250-260C.

While the invention is particularly useful for printing on a printed circuit board, it may also be used in marking of additional types of substrates such as lithographic printing plates or panels of electrical and electronic appliances.

These and other advantages of the present invention will become more apparent from the summary of the invention and detailed description of the invention that follow.

SUMMARY OF THE INVENTION

The present invention relates to a heat curable ink composition for printing on printed circuit boards or any other suitable substrate using an ink jet printer,

comprising at least one non-aqueous solvent, a pigment, a melamine based resin system, at least one additive, and at least one dispersing agent. The melamine based resin system comprises a crosslinking agent and a polymer capable of reacting with said crosslinking agent.

According to preferred embodiments of the present invention, the solvent is an organic solvent selected from one or more of the group consisting of: propylene carbonate, butylrolactone, various glycol ethers such as: propylene glycol methyl ether, propylene glycol methyl ether acetate, dipropylene glycol methyl ether, glycerol, tetraethylene glycol, ethylene glycol, and propylene glycol. Preferably, the solvent is a combination of one or more of the aforementioned list. The concentration of each solvent in the solvent mixture is selected in order to achieve optimal overall viscosity, surface tension and volatility.

Moreover according to preferred embodiments of the present invention, the solvent mixture is present in an amount of about 40-80% by weight of ink composition.

Additionally according to preferred embodiments of the present invention, the pigment has a particle size of less than 2 micron. This facilitates jetting without the ink clogging the printer nozzles. Preferably, the pigment has a particle size of less than 0.4 micron. The pigment may comprise organic or inorganic particles, depending on the required color.

Further according to preferred embodiments of the present invention, the pigment is present in an amount of about 10-50% by weight of the ink composition. The concentration of the pigment is selected in such a way which enables obtaining the required viscosity-temperature profile, and also the proper hiding power and optical density. For example, if a white legend ink is required, the preferred pigment is titanium dioxide, having a particle size in the range of 0.17-0.3 micrometer, and weight concentration of about 15-35%. In addition, in order to achieve the required optical density and hiding power, the ink may contain, in addition to the pigment, functional fillers (often called "extenders"), such as fumed silica, clays and zeolites. Examples of such functional fillers are Aerosil 200, Aerosil 972, (Degussa), HDK H15P (Wacker HDK), CAB-O-SIL TS-350 (CABOT), ASP Ultrafine (Engelhard), Burgess 99, Burgess 10 (Burgess) and Zeolex 98 (Huber Eng. Materials).

Still further according to preferred embodiments of the present invention, the

melamine based resin system comprises at least one hydroxyl containing polymer, and at least one melamine derivative capable of crosslinking said polymer. Preferably, the polymer is present in an amount of about 5-45% by weight of the ink composition and the melamine derivative is present in an amount of about 5-45% by weight of the ink composition. The polymer and the melamine derivative are in a ratio, for example of between 70:30 to 30:70 (polymer: melamine derivative). The system undergoes a cross-linking reaction after short heating of about 15-30 minutes at 130-160 degree. C.

Moreover according to preferred embodiments of the present invention, the polymer comprises an alkyd, or polyester, or acrylic resin, having the ability to react with the melamine derivative.

Additionally according to preferred embodiments of the present invention, the ink composition also comprises a basic inhibitor. Preferably, the basic inhibitor is an amine having a high boiling point and may be selected from the group consisting of diethanolamine, methyldiethanolamine, 2-amino2-methyl1-propanol, and monoethanolamine. Preferably, the basic inhibitor is present in an amount of about 0.1-5% by weight of the ink composition. The basic inhibitor is selected in such a way which would allow it to inhibit the crosslinking reaction at temperatures up to the temperature in which the printhead operates, but stops the inhibition at elevated temperatures (curing temperature) mostly due to it's evaporation from the ink.

Further according to preferred embodiments of the present invention, the additive is a rheological additive. Preferably, the rheological additive is selected from one or more of the group consisting of polyurea solutions, polyhydroxycarboxylic acid amides, submicron silicas, clays and clay derivatives, cellulose derivatives, and polyamine polymers. The rheological addititives (in addition to the appropriate solvent mixture) serves to ensure that the ink composition has the appropriate viscosity during jetting of the ink and during setting of the ink on the PCB.

Still further according to preferred embodiments of the present invention, the ink composition has a Brookfield viscosity of 30-100cps at 25 degree. C. and a Brookfield viscosity of 10-20cps at 50-80 degree. C. (at 10-20 rpm, Spindell).

Moreover according to preferred embodiments of the present invention, the ink composition further comprises at least one wetting agent. Preferably, the wetting agent is present in an amount of about 0.01-5% by weight of the ink composition.

Additionally according to preferred embodiments of the present invention, the dispersing agent is selected from the group consisting of dispersants with acidic groups, dispersants with amine groups, a high molecular weight anionic, cationic and nonionic polymer and polycarboxylic acid with amine derivatives. Preferably, the dispersing agent is present in an amount of about 0.5-10% by weight of the ink composition.

Moreover according to preferred embodiments of the present invention, the pigment comprises one or more metal oxides. Preferably, the pigment is selected from titanium dioxide or titanium dioxide coated with functional groups. Alternatively, the pigment comprises iron oxide particles.

Further according to preferred embodiments of the present invention, the additive comprises a functional filler aimed at achieving better hiding power and optical density. Preferably, the functional filler is selected from submicron silica, clays, zeolytes, and mixtures thereof.

The present invention also relates to a method for printing a legend onto a printed circuit board comprising ink jet printing the heat curable ink composition described above onto the printed circuit board. Following the printing step, the PCB is cured at a temperature of about 130-160 degree. C for 15min to 1 hour.

The present invention also relates to a heat curable ink composition for printing on printed circuit boards using an ink jet printer, comprising a solvent mixture in an amount of about 40-80% by weight of the ink composition, a pigment in an amount of about 10-50% by weight of the ink composition, a hydroxyl containing polymer in an amount of about 5-45% by weight of the ink composition, a melamine derivative capable of cross linking said polymer in an amount of about 5-45% by weight of the ink composition, a basic inhibitor in an amount of about 0.1-5% by weight of the ink composition, a dispersing agent in an amount of about 0.5-10% by weight of the ink composition, a rheological additive in an amount of about 0.1-5% by weight of the ink composition, and a wetting agent in an amount of about 0.01% by weight of the ink composition.

The present invention also relates to a method for printing a legend and/or at least one pattern onto a printed circuit board comprising ink jet printing the heat curable ink composition described above onto the printed circuit board. Following the printing step, the PCB is cured at a temperature of about 130-160 degree. C for 15min

to 1 hour.

DETAILED DESCRIPTION OF THE INVENTION

The components of the heat curable ink composition will now be described, and certain examples provided, for the purposes of example and clarification only.

The ink solvent is preferably selected from organic solvents possessing different viscosities, surface tensions, and vapor pressures. The solvents may be selected from: propylene carbonate, butyrolactone, glycol ethers such as: propylene glycol methyl ether (PM), propylene glycol methyl ether acetate (PMA), dipropylene glycol methyl ether (DPM), glycerol, tetraethylene glycol, ethylene glycol, propylene glycol, or any appropriate combination thereof. The combination of solvents preferably includes solvents having medium volatility (DPM) and very low volatility (glycerol, tetrathylene glycol, propylene carbonate, propylene glycol, tripropyleneglycol momomethyl ether, and others). This prevents evaporation of solvents on the nozzle plate of the print head, which can lead to clogging. As an example, the combination of solvents may be PMA, DPM, propylene carbonate, tetrathylene glycol, and glycerol. Alternatively, the combination of solvents may be PMA, PM, propylene carbonate, tetrathylene glycol, and glycerol. Preferably, the solvents comprises about 40-80% by weight of the ink composition.

The pigment may comprise any appropriate organic or inorganic particles, depending on the required color (in the context of the present disclosure, the term "pigment" is meant to refer to any to any colorant, dye, or pigment that may be dissolved or dispersed in the ink). As an example, white legend ink can be formulated from fine titanium oxide particles, such as Kronos 2300, 2310, Kemira 650, and others. The pigments suitable for use in the ink composition of the present invention preferably have a particle size of less than 2 micron and more preferably, less than 0.4 micron. The concentration of the pigment can vary according to the required final optical density or hiding power. Preferably, the pigment is present in an amount of about 10-50% by weight of the ink composition. The pigment may be coated by functional groups, for example to prevent photocatalytic activity, to change the surface hydrophobicity etc.

The melamine based resin system is based on a mixture of an alkyd, polyester, or acrylic resin, in combination with a melamine or melamine resin and amine

inhibitor. Such resin systems are well known in the art and may be selected, for example, from branched saturated polyester, such as Crodapol O-16 (made by Croda), mixed with a melamine formaldehyde resin, such as Beetle BE 76 or BE 683 (made by BIP) or Cymel 325 (made by Cytec) at a ratio of 70:30 to 30:70. Another example is Crodapol O-14 (a slightly branched saturated polyester) mixed with hexa-methoxy methyl-melamines at rations between 70:30 and 30:70 (polymer: amino). In the examples, the solution of the melamine based resin system, which is the mixture of melamine derivatives, the polymers and the basic inhibitor, is referred to as the "melamine varnish".

The rehological additive may be selected from polyurea solutions capable of building a tri-dimensional net, such as BYK 410, BYK 411 (from BYK Chemie), polyhydroxycarboxylic acid amides, BYK 405 (from BYK Chemie), micronized silicas such as Aerosils, polyamine polymers such as Thixatrol (from Rheox), cellulose derivatives, and others. The rehological characteristics of the ink (achieved through the use of the proper selection and concentration of the solvent and pigment, as well as the rheological additives described) ensures good jetting of the ink from the print head, and proper fixation of each ink droplet into its appropriate position. An additional benefit of the rheological properties is the slowing of the sedimentation of pigment particles during storage, which is a common problem in low viscosity paints containing titanium oxide pigments.

The dispersing agent(s) is preferably selected from a polymer containing groups with high affinity to the pigment surface, for example acidic groups, such as Disperbyk 110 (from BYK Chemie), or a high molecular weight block copolymer with pigment affinic groups, such as Disperbyk 168 (from BYK Chemie). Other possible dispersing agents include EFKA 1800, and Texaphor 963 (from Henkel) which is a polycarboxylic acid containing amine derivatives, and others.

Wetting agents may be selected from BYK 358, BYK 354 (both from BYK Chemie) and other appropriate high molecular weight additives that serve to improve the coalescence between adjacent ink droplets without decreasing the surface tension of the ink composition. This prevents surface problems such as dewetting, "fish eyes", and others and helps to achieve smooth surfaces.

The basic inhibitor is an amine having a high boiling point and may be selected from the group consisting of diethanolamine, methyldiethanolamine,

2-amino 2-methyl1-propanol, and monoethanolamine. Preferably, the basic inhibitor is present in an amount of about 0.1-5% by weight of the ink composition.

Reference should be made to Tables 1 and 2 below for examples of the ink composition of the present invention. Examples of 14 different compositions (A-N) are provided and the numbers represent the amount by weight in the ink composition of the respective component. All of the ink compositions gave satisfactory results after being tested using a Spectra print head and cured at a temperature of 130-160 degree C for 15min-1 hr. The printing quality (readability) was very good, and the printed legends have unique resistance to very high temperatures, dipping in solvents and solder bath, and met all the extreme requirements from a PCB legend ink.

Table 1: Formulation Examples A-G

	A	B	C	D	E	F	G
Melamine Varnish	17.17	21.04	21.00	20.94	20.64	20.59	21.3
Disperbyk 110(1)	1.84	1.51	1.51	1.50	1.48	1.48	1.5
Disperbyk 107(1)				0.30			
PMA	4.25	5.04	5.03	5.02	5.13	5.13	4.9
DPM	10.97	12.47	12.44	12.40	12.71	12.68	12.2
Propylene Carbonate	23.21	26.53	26.47	26.39	27.05	26.99	26.0
Tetrathylene Glycol	1.83	1.92	1.92	1.92	1.89	1.88	1.95
Glycerol	0.97	0.96	0.96	0.95	0.94	0.94	1.0
Pluronic F-127(2)	0.20		0.20	0.20	0.20	0.20	0.20
BYK 410(1)	0.35	0.35	0.35	0.35		0.60	
Fumed silica					2.0	0.5	0.8
Titanium Oxide(3,4,5)	39.21	30.19	30.13	30.03	28.0	29.0	30.0
	100	100.01	100.00	100.00	100.00	100.00	100.00

Table 2: Formulation Examples H-N

	H	I	J	K	L	M	N
Melamine Varnish	23.94	24.51	23.87	23.86	23.94	23.94	23.94
Disperbyk 110(1)	1.31	1.34	1.3	1.3	1.31	1.31	1.31
PMA	1.69	1.73	1.68	1.68	1.69	1.69	1.69
PM	14.35	12.65	14.31	14.3	14.35	14.35	14.35
Propylene Carbonate	24.2	24.78	24.13	24.11	24.2	24.2	24.2
Tetrathylene Glycol	4.76	4.87	4.75	4.74	4.76	4.76	4.76
Glycerol	2.51	2.57	2.51	2.51	2.51	2.51	2.51
BYK358(1)	0.2	0.2				0.2	0.2
Fumed silica		1.0	0.5				
BYK 410(1)	0.34		0.34	0.9	0.34	0.34	0.34
Titanium Oxide(3,4,5)	26.41	26.05	26.33	26.31	26.4	26.41	26.41
Pluronic F-127(2)	0.19	0.2	0.19	0.19	0.4	0.19	0.19
Texaphor 963(6)	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	100	100	100	100	100	100	100

(1) BYK Chemie
(2) BASF
(3) Kronos 2310
(4) Tioxide TR92
(5) Kemira 650
(6) Cognis

All of these inks were tested in a Spectra ™ printhead, and gave satisfactory results. The optimal composition can be selected according to the printer requirements, and the type of printed circuit boards onto which the ink is printed.

CLAIMS

1. A heat curable ink composition for printing on a substrate using an ink jet printer, comprising at least one non-aqueous solvent, at least one pigment, a melamine based resin system, at least one additive, and at least one dispersing agent, wherein said melamine based resin system comprises a crosslinking agent and a polymer capable of reacting with said crosslinking agent.

2. A heat curable in composition according to claim 1, wherein said substrate is a printed circuit board.

3. A heat curable ink composition according to claim 1, wherein said at least one solvent is an organic solvent selected from one or more of the group consisting of: propylene carbonate, butylrolactone, glyco eters such as: propylene glycol methyl ether, propylene glycol methyl ether acetate, dipropylene glycol methyl ether, glycerol, tetraethylene glycol, ethylene glycol, and propylene glycol.

4. A heat curable ink composition according to claim 3, wherein said solvent is present in an amount of about 15-80% by weight of ink composition.

5. A heat curable ink composition according to claim 1, wherein the pigment has a particle size of less than 2 micron.

6. A heat curable ink composition according to claim 5, wherein the pigment has a particle size of less than 0.4 micron.

7. A heat curable ink composition according to claim 1, wherein the pigment is present in an amount of about 10-50% by weight of the ink composition.

8. A heat curable ink composition according to claim 1, wherein the melamine based resin system comprises at least one hydroxyl containing polymer, and at least one melamine derivative capable of crosslinking said polymer.

9. A heat curable ink composition according to claim 8, wherein the polymer is present in an amount of about 5-45% by weight of the ink composition.

10. A heat curable ink composition according to claim 8, wherein the melamine derivative is present in an amount of about 5-45% by weight of the ink composition.

11. A heat curable ink composition according to claim 8, wherein the polymer comprises an alkyd, polyester, or acrylic resin.

12. A heat curable ink composition according to claim 1, further comprising a basic inhibitor.

13. A heat curable ink composition according to claim 12, wherein the basic

inhibitor is an amine having a high boiling point.

14. A heat curable ink composition according to claim 13, wherein the basic inhibitor is selected from the group consisting of diethanolamine; methyldiethanolamine; 2-amino,2-methyl,1-propanol and monoethanolamine.

15. A heat curable ink composition according to claim 14, wherein the basic inhibitor is present in an amount of about 0.1-5% by weight of the ink composition.

16. A heat curable ink composition according to claim 1, wherein said at least one additive is a rehological additive.

17. A heat curable ink composition according to claim 16, wherein the rheological additive is selected from one or more of the group consisting of polyurea solutions, polyhydroxycarboxylic acid amides, micronized silicas, and polyamine polymers.

18. A heat curable ink composition according to claim 1, wherein said ink composition has a Brookfield viscosity of 30-100cps at 25 degree. C. and a Brookfield viscosity of 10-20cps at 50-80 degree. C.

19. A heat curable ink composition according to claim 1, further comprising at least one wetting agent.

20. A heat curable ink composition according to claim 19, wherein the wetting agent is present in an amount of about 0.01-5% by weight of the ink composition.

21. A heat curable ink composition according to claim 1, wherein said at least one dispersing agent is selected from the group consisting of dispersants with acidic groups, dispersants with amine groups, a high molecular weight anionic, cationic and nonionic polymer and polycarboxylic acid with amine derivatives.

22. A heat curable ink composition according to claim 21, wherein the dispersing agent is present in an amount of about 1-10% by weight of the ink composition.

23. A heat curable ink composition according to claim 1, wherein the pigment comprises one or more metal oxides.

24. A heat curable ink composition according to claim 23, wherein the pigment is selected from titanium dioxide or titanium dioxide coated with functional groups.

25. A heat curable ink composition according to claim 23, wherein the pigment comprises iron oxide particles.

26. A heat curable ink composition according to claim 1, wherein the additive comprises a functional filler aimed at achieving better hiding power and optical density.

27. A heat curable ink composition according to claim 26, wherein the said functional filler is selected from submicron silica, clays, zeolytes, and mixtures thereof.

28. A method for printing onto a printed circuit board comprising ink jet printing the heat curable ink composition of any one of the preceding claims onto said printed circuit board.

29. A heat curable ink composition for printing on printed circuit boards using an ink jet printer, comprising at least one non-aqueous solvent in an amount of about 15-80% by weight of the ink composition, a pigment in an amount of about 10-50% by weight of the ink composition, a hydroxyl containing polymer in an amount of about 5-45% by weight of the ink composition, a melamine derivative capable of cross linking said polymer in an amount of about 5-45% by weight of the ink composition, a basic inhibitor in an amount of about 0.1-5% by weight of the ink composition, a dispersing agent in an amount of about 0.5-10% by weight of the ink composition, a rheological additive in an amount of about 0.1-5% by weight of the ink composition, and a wetting agent in an amount of about 0.01% by weight of the ink composition.

30. A method for printing a legend onto a printed circuit board comprising ink jet printing the heat curable ink composition of claim 29 onto said printed circuit board.